SIMULATIONS OF X-RAY PHOTOELECTRON DIFFRACTION EXPERIMENT FROM THEORETICAL CALCULATIONS

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In this paper, we demonstrate the simulation of XPD experiments through theoretical calculations. We present examples, e.g. oxygen-induced Cu(210) surface and oxygenated diamond surface, to illustrate how to obtain the optimized XPD experimental parameters by MSCD simulations for distinguishing two different models. Our results suggest that for the adsorbate-induced reconstructions on metal or semiconductor surfaces, XPD from adsorbate is more sensitive to the detailed surface structure than XPD from bulk elements. Whether to choose energy-scanned or angle-scanned mode will depend on the systems under investigation. One should check any limitations in the instruments used, and then perform the theoretical simulations for typical available parameters in order to select the best mode, emitters, and optimized parameters.

1. Introduction

There has been much growth in surface science research in recent years with the development of new experimental techniques as well as theoretical modeling calculations. Most available modeling programs have been developed for simulating experimental results, e.g. low energy electron diffraction (LEED)[1] and X-ray photoelectron diffraction (XPD).[2] However, experiments are often performed in a time-consuming trial-and-error process or by choosing most convenient experimental parameters. On the other hand, due to the limitations in the simulation programs used, different models sometimes present comparable best-fit results. For example, tensor LEED studies on an oxygen-induced Cu(210) surface reveal two different models for the (2×1) reconstruction with similarly small Pendry reliability factors against the same IV LEED experimental data. Hence, the optimization of the experimental process to distinguish different models is important.

From the theoretical point of view, it is possible to employ state-of-the-art computational tools [e.g. the multiple-scattering calculation diffraction (MSCD) method[3]] to simulate real XPD data and obtain optimized experimental parameters to distinguish two competing models.

In this paper, we present two examples, the Cu(210)–O surface and oxygenated diamond surface, to illustrate how we obtain the optimized XPD experimental parameters by MSCD simulations. We also present the XPD pattern of B-terminated and N-terminated cubic BN(001) surface by MSCD calculations.

2. Methods of Calculations

In this study, the MSCD package for XPD calculation is used to simulate XPD experimental results from tentatively proposed structures. The MSCD package was developed by Chen and Van Hove with several collaborators.[3] This program simulates the elemental and state-specific core-level photoelectron diffraction pattern from a surface, based on multiple scattering theory and the Rehr–Albers separable

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representation of spherical-wave propagators, and by fitting to experimentally determined atomic structural information. The multiple-scattering (MS) order $n_{max} = 8$ and Rehr–Albers (RA) approximation order $|\mu|_{max} = 4$ are used in all simulations. Suitable cluster sizes of about 100–150 atoms have been shown to be adequate for representing ideal surfaces of metal or semiconductors.[3] We note that in Wu and Tong's recent work,[4] they used Ni(001) as an example, and found that when $n = 253$ atoms, the convergence of the two methods (RI method and slab method) could be achieved. The reference where the MSCD code is first discussed[3] presented the testing of cluster size and concluded that the clusters of about 100 atoms in size should be sufficient for most problems, in agreement with prior studies.[5] Chen *et al.* used several sizes (i.e. 44, 77, 119, 179 atoms) of Cu(111) clusters as an example to test the convergence of the calculations and found that a 119-atom cluster yielded most of the peaks and valleys at proper locations. To confirm our calculations, the convergence for Cu(210) using MSCD code is now tested. We have calculated the chi function (energy scan) for two models of Cu(210)-(2×1)O (O 1s as emitter) as a function of cluster size (e.g. 91, 163, 256 atoms) and found that the chi function is not changed by much. The R-factors (the difference between two models) only slightly change as a function of cluster size, for example, the R-factors reduce by 0.005 after the cluster sizes increase from 91 atoms to 163 atoms, and by 0.01 when the sizes increase from 91 atoms to 256 atoms. Comparing with the R-factors for O 1s emission in Tables 1 and 2, this reduction due to the effect of cluster size is rather small and can be neglected. Thus the effect of cluster size will not change our conclusions in the paper.

The MSCD package has been used to simulate actual experimental data, e.g. on surfaces of W(110), O/W(110), Li/Al(111) and MnO(100), etc.[3] Some of other applications of MSCD code can be found at Ref. 6. Studied examples include: Ni(001)+c(2×2)-S/S1s, Fe(001)+c(2×2)-P/P1s, clean Cu(111)-3s and 3p and Ni(111)-3p;[6(a)] Fe/Ni(001) films;[6(b)] interaction of Se and GaSe with Si(111).[6(c)] More recently, this package has also been used to study the more complicated surface of AlPdMn quasicrystal.[7] Extensive testing[3] and successful applications[3,6,7]

Table 1.   The R-factors (show the differences between two models) of Cu(210)–O (2×1) surface.

Modes	O 1s	Cu 2p	Cu 3s
Angle-scanned	0.4590	0.0128	0.0110
Energy-scanned	0.1801	0.0098	0.0123

Table 2.   The R-factors of Cu(210)–O (2×1) surface (LBR-MS model) with different position of oxygen in vertical direction. (Assuming model "A" as reference.)

	Modes	O 1s	Cu 2p	Cu 3s
B	Angle-scanned	0.1008	0.0019	0.0015
	Energy-scanned	0.3088	0.0293	0.0057
C	Angle-scanned	0.1041	0.0010	0.0394
	Energy-scanned	0.2957	0.0468	0.0619

indicate the high accuracy and capacity of this package for treating complex systems. Therefore, MSCD can be used as a reasonable tool for the photoelectron diffraction simulation study.

3.   Approach for Designing XPD Experiments

The XPD experimental setup is shown in Fig. 1. In normal experiments, the researchers select several experimental parameters that will best discriminate between proposed models of the surface. This is done by considering the following questions:

 (i) Since XPD is element-specific, which element and which angular momentum for a chosen element should be chosen for investigation?
 (ii) Which mode will be more suitable for the systems under investigation — energy-scanned mode or angle-scanned mode?
(iii) For energy-scanned mode, which are the best geometrical parameters to be used, such as the incident angle and the polarization of X-rays (for synchrotron radiation), the angle between
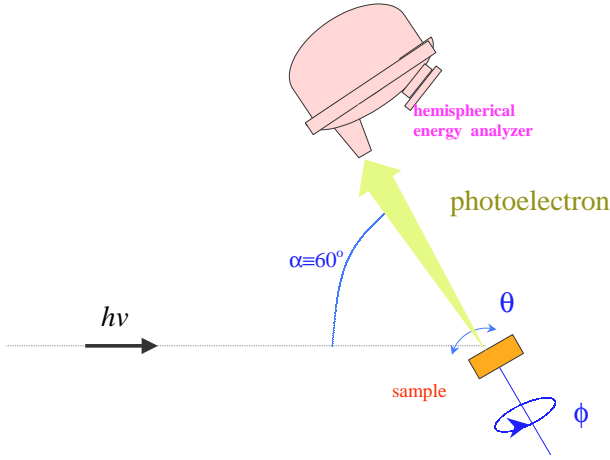
Fig. 1. Experimental setup of typical XPD (X-ray photoelectron diffraction).

sample and X-ray, sample and detector, X-ray and detector? Sometimes, one will want to compare the energy-scanned XPD at different theta or phi angles, so how does one select the value of theta or phi?

(iv) For angle-scanned mode, which energy range is more suitable for distinguishing two possible structures? How does one decide whether to perform theta angle or phi angle-scanned XPD or full angle-scanned XPD?

(v) Other incidental considerations are the temperature of the sample, the limitation of the light sources (laboratory X-ray or synchrotron radiation), the limitation of instruments (capability to rotate the samples or detectors).

In this paper, we will briefly discuss ideas on how to plan XPD experiments from theoretical simulation. In particular, we present several examples to illustrate the design of real XPD experiments for distinguishing two competing models by obtaining the optimized parameters from MSCD simulation. Our motivation is the knowledge that experimentalists often use a error-and-trial process or adopt the most convenient experimental parameters for their specific investigation of given samples, while theoretical simulations can be easier, quicker and cheaper way to determine the best (or at least reasonable) parameters.

Our idea of how to design the experimental parameters for distinguishing two competing models can be summarized as follows:

(a) Calculate the XPD intensity for the two different models (e.g. models "A" and "B") with the same experimental parameters using the MSCD package.

(b) Compute the difference between the intensities for the two models by calculating the reliability factors (R-factors) defined by the following equation:[3]

$$R = \sum_i \frac{(\chi_{Ai} - \chi_{Bi})^2}{\chi_{Ai}^2 + \chi_{Bi}^2}, \qquad (1)$$

where χ_{Ai} and χ_{Bi} are χ curves for models "A" and "B" respectively. Here, χ curves are defined[3] as

$$\chi = (I - I_0)/I_0, \qquad (2)$$

where I is the photoemission intensity and I_0 is the background intensity. For the energy-scanned mode, the background is subtracted from the intensity versus wave number curve by using a spline fitting method. For the angle-scanned mode, the background is subtracted from the intensity versus phi angle curve by a linear fitting method, and versus theta angle curve by the spline fitting method.

(c) Obtain the relationship between R-factors and several experimental parameters. Large R-factors indicate large differences between two models with respect to certain parameters, so that it will be better to perform the experiment under such conditions to distinguish the two models. Parameters which give small R-factors will conversely not be suitable for distinguishing the two models.

4. Examples and Discussions

4.1. *Example I: Cu(210)–O (2 × 1) system*

Recently, tensor LEED[1] studies on an oxygen-induced reconstructed Cu(210) surface[8] reveal two different models (as shown in Fig. 2) for the (2 × 1) reconstruction with similarly low Pendry R-factors against the same IV LEED experimental data. The combination of LEED with other techniques such as STM, SEXAFS and XPD can distinguish these two similar best-fit structures. It is sometimes possible to use first principles calculations to determine which
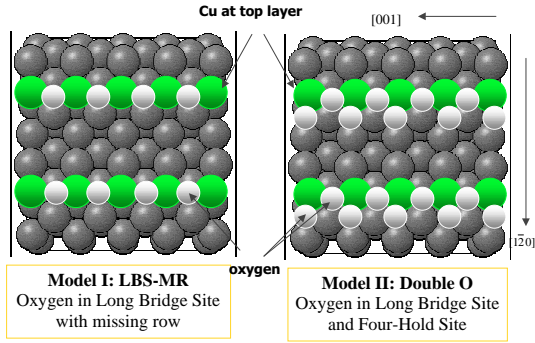
Fig. 2.   Two models of oxygen-induced (2×1) Cu(210) surface. Both models are best-fit structures for Cu(210) surface with 15 L oxygen uptake at 550 K.

one is more stable by comparing their total energy. Here, we consider XPD only and discuss the conditions under which one can distinguish these two models.

Figure 3 shows the XPD pattern of the Cu(210)–O (2×1) surface simulated by the MSCD PD package by both angle-scanned mode and energy-scanned mode for Cu 3s and 2p and O 1s core levels. The R-factors (showing the differences between two models) are listed in Table 1. From Fig. 3 and Table 1, one can see that the R-factors for O 1s are larger than that for Cu 2p and Cu 3s core levels. This means that the differences between the two models
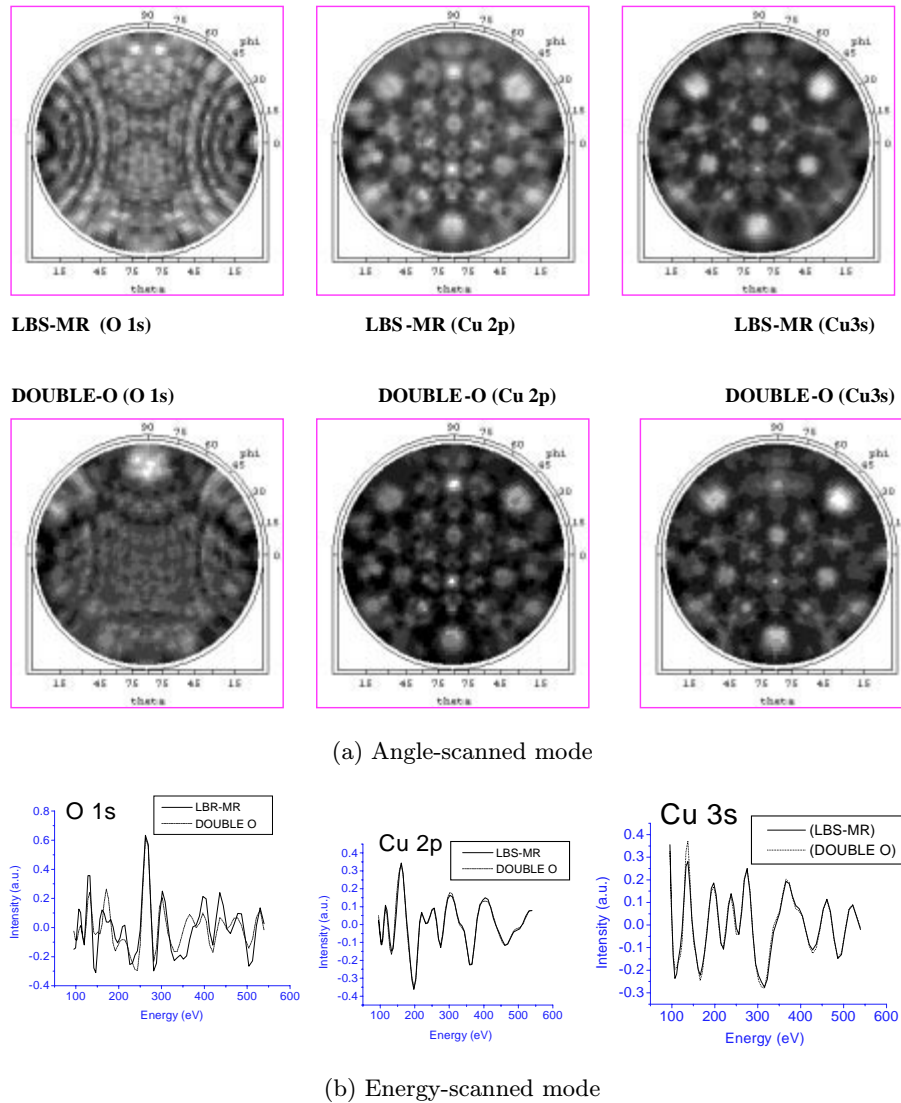

(a) Angle-scanned mode

(b) Energy-scanned mode

Fig. 3.   XPD pattern of Cu(210)–O (2×1) surface simulated by MSCD PD package.   (a) Angle-scanned mode; (b) energy-scanned mode.
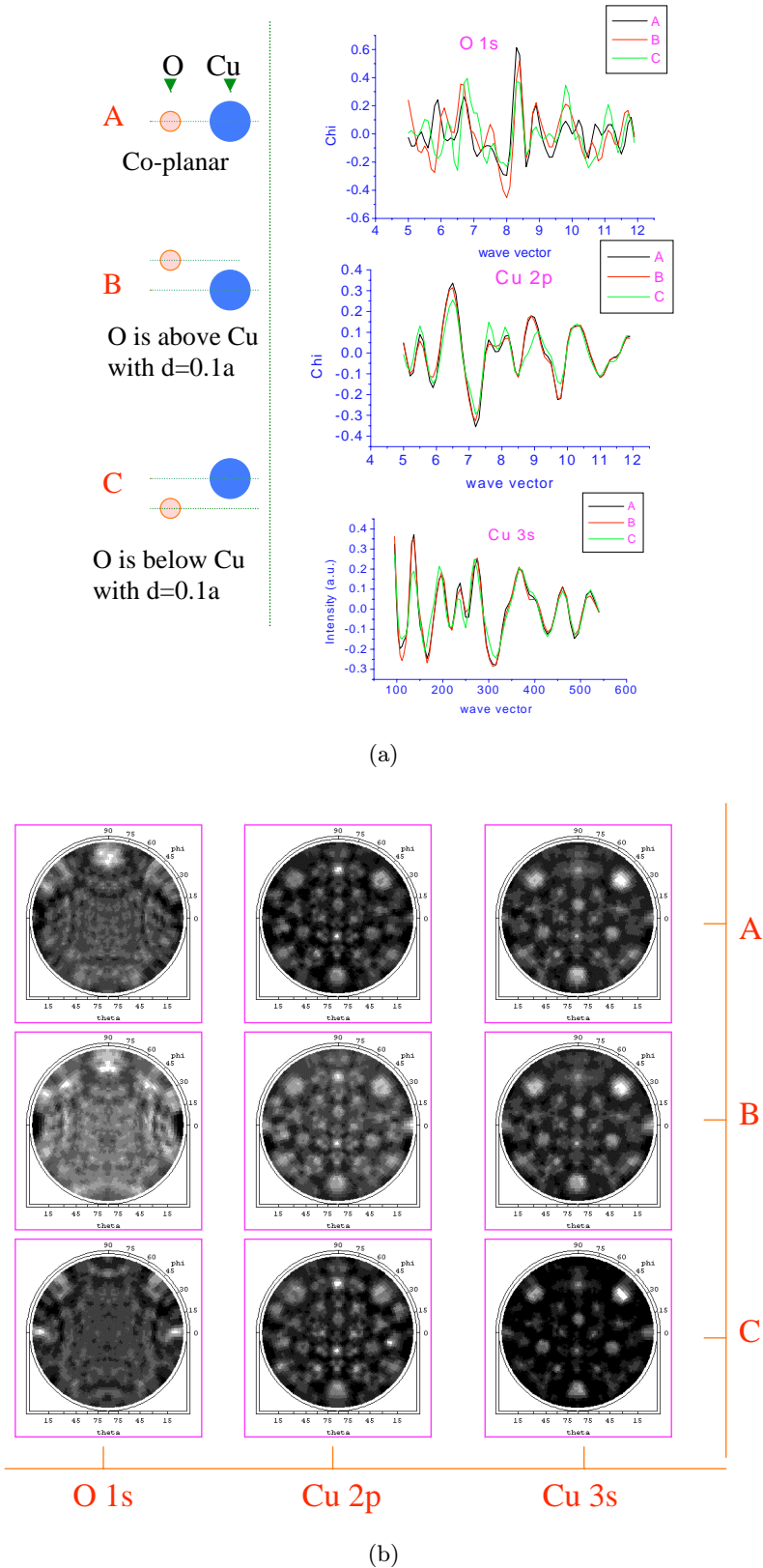
(a)

(b)

Fig. 4.   XPD patterns of Cu(210)–O (2×1) system (LBS-MR model) with different position of oxygen in vertical direction. (a) Energy-scanned mode; (b) angle-scanned mode.

can be easily detected from the oxygen XPD pattern. We also note that the angle-scanned mode shows a larger R-factor than the energy-scanned mode. Our results suggest that for the Cu(210)–O (2×1) system, it would be better to perform the XPD experiment in angle-scanned mode using O 1s emission to distinguish between the two models of Fig. 2. However, if one needs to know whether oxygen is located coplanar with or above or below the topmost Cu atoms (as shown in Fig. 4), it is obvious that the energy-scanned mode for O 1s will be best, as indicated by the large R-factor in Table 2.

4.2.   Example II: oxygenated diamond (100) surface

There are also two possible oxygenated diamond (100) surface models as suggested by first principles calculations,[9,10] named the "bridge" and "on-top" models, as illustrated in Fig. 5. The simulated

Model I: Bridge Model   Model II: Double-bonded Model (On-top model)
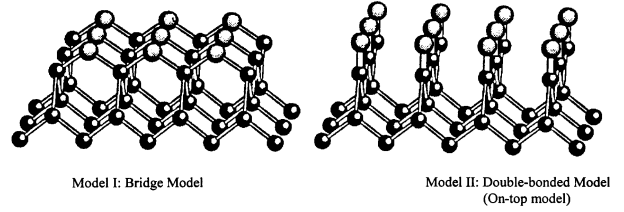
Fig. 5.   Two models of oxygenated diamond (100) surface.

angle-scanned and energy-scanned XPD patterns are shown in Fig. 6. It is clear that the energy-scanned mode is more discriminating than the angle-scanned mode.

4.3.   Example III: bulk cubic BN surface

For bulk cubic BN surface, we only show the XPD pattern for the BN(100) 1×1 ideal case since no any experimental data is yet available for detailed
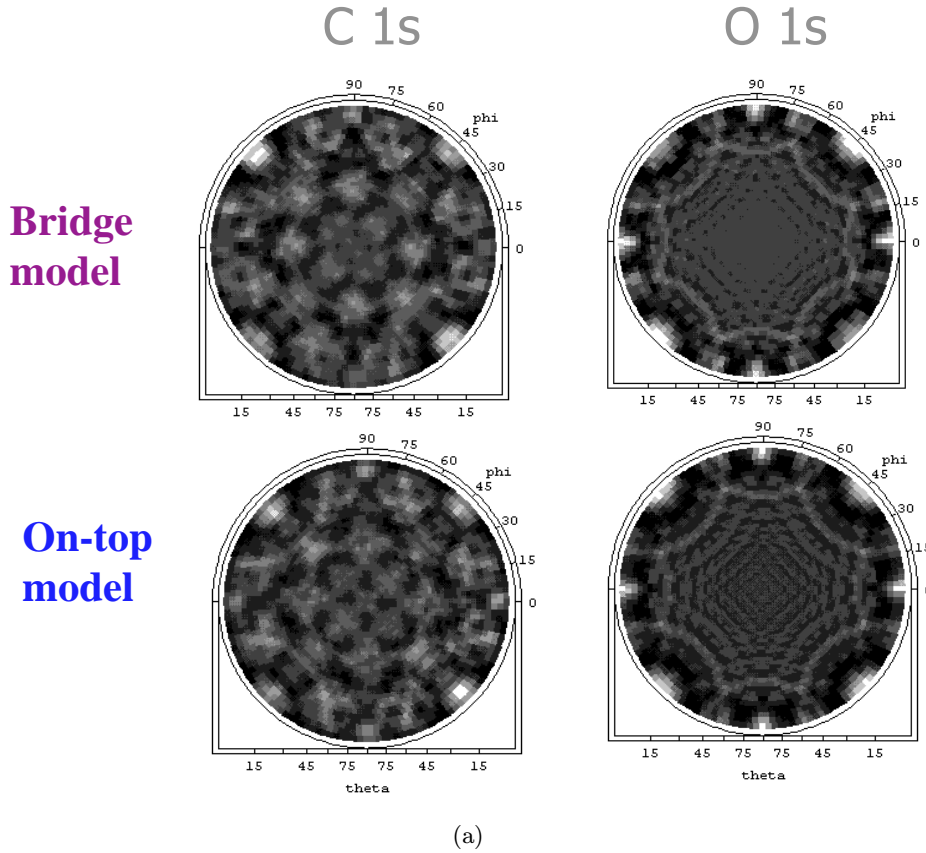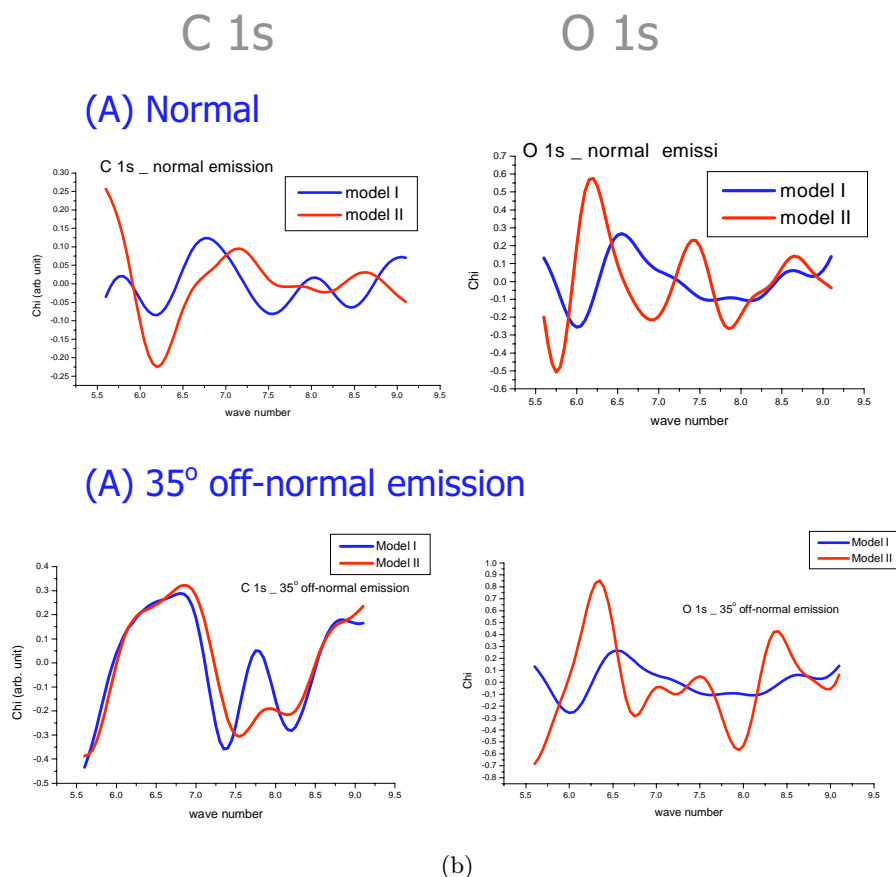

(a)

Fig. 6.   XPD pattern of two models of oxygenated diamond (100) surface. (a) Angle-scanned mode; (b) energy-scanned mode. Model I is the bridge model, and model II is the on-top model.

Fig. 6. (*continued*)

BN(100) surface. Here, we consider both the B-terminated and N-terminated surfaces. We then calculate the XPD patterns for photoemissions from B 1s and N 1s core levels. The results are shown in Fig. 7 for angle-scanned mode. It can be seen that the B 1s core level XPD pattern of the B-terminated BN (100) surface is quite similar to the N 1s core-level XPD pattern of the N-terminated BN surface. The same is true for the B 1s XPD of N-terminated and N 1s of B-terminated BN surface. This is because they share similar directions between emitters and scatterers. The spots in the XPD pattern indicate the directions between emitters and scatterers on the surface.

5. Conclusion

In summary, we have used two examples, i.e. Cu(210)-(2 × 1)O and oxygenated diamond (100) surfaces, to illustrate how the XPD experiment should be optimized to distinguish between two possible (or LEED best-fit) surface structures. For the adsorbate-induced reconstruction on metal or semiconductor surfaces, XPD of the adsorbate will be more sensitive to the detailed surface structure than that of bulk elements. The choice of energy-scanned or angle-scanned mode will depend on the system under investigation. For the Cu(210)–O (2 × 1) surface for example, the angle-scanned mode will be more sensitive to two different models rather than the energy-scanned mode. Conversely, to distinguish the position of oxygen in the vertical directions, the energy-scanned mode appears to be more suitable. For the oxygenated diamond (100) surface, our results show that the energy-scanned mode will be easier to distinguish the "bridge" and "on-top" models than the angle-scanned mode. Hence, we suggest that any constraints in the instruments used should first be considered, and the theoretical simulations for some typical available parameters
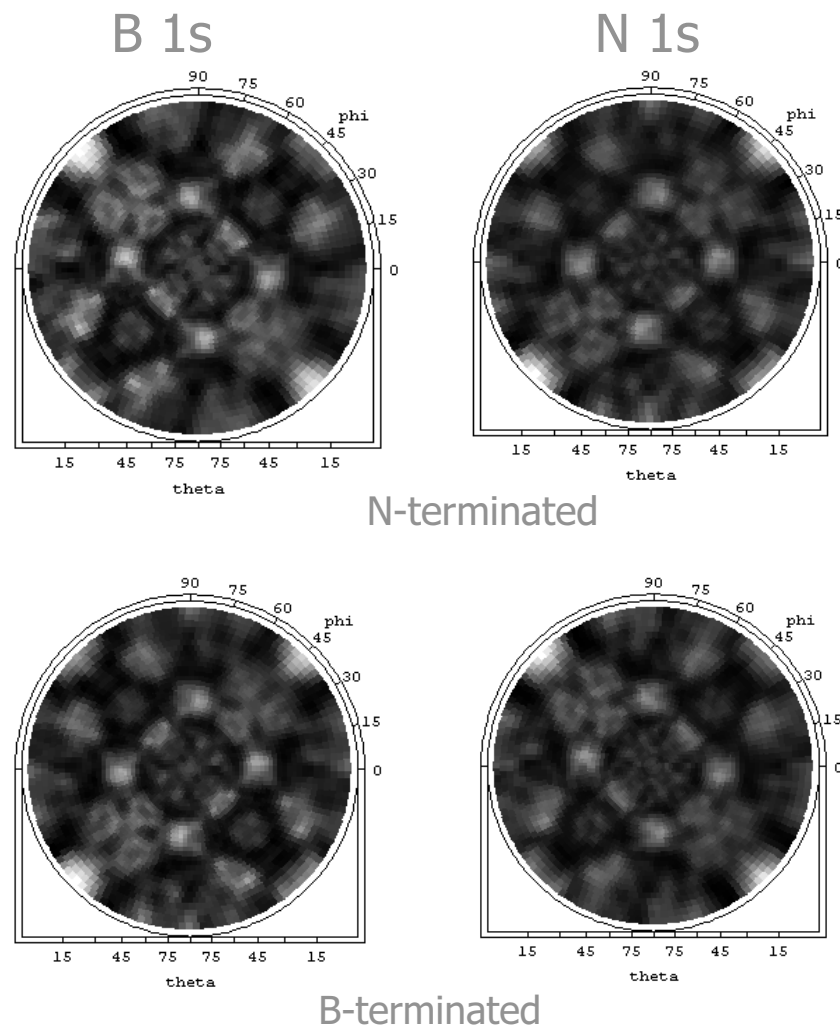
B 1s

N 1s

N-terminated

B-terminated

Fig. 7.   XPD pattern of cubic BN (100) surface with B- or N-terminated.

performed to determine the optimized mode, emitters, and parameters.

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